"Express Mail" mailing label number:

EV 335895890 US

OPTICAL SPINEL ARTICLES AND METHODS FOR FORMING SAME

Jennifer Stone-Sundberg
Milan Kokta

CROSS-REFERENCE TO RELATED APPLICATION(S)

[0001] This application is a continuation-in-part of and claims priority to US Application Number 10/669,141, filed September 23, 2003 (attorney docket number BI4282), and hereby incorporates by reference the subject matter of that application.

BACKGROUND

Field of the Invention

[0002] The present invention is generally directed to materials and articles having a spinel crystal structure. In addition, the present invention relates generally to spinel materials particularly useful for optical applications.

Description of the Related Art

[0003] Various aluminous materials have been used and/or evaluated for demanding optical applications. Such optical applications include, for example, high powered lasing applications, in which the optical material is utilized as a window or mirror, through which an optical laser beam may be passed or reflected. Aluminous materials that have been under consideration include single crystal alumina, typically in the form of sapphire. Other materials are microstructurally distinct from alumina, but containing a substantial portion of alumina groups, including yittria alumina garnet (YAG), as well as spinel ($MgO{\cdot}Al_2O_3$). While sapphire and YAG demonstrate certain levels of robustness, the art continually demands materials having superior performance. In addition, sapphire does not have an optically isotropic structure, and accordingly, careful attention must be paid

during fabrication of components to properly align the microstructure with the intended axis of the light passing through the component.

[0004] Spinel-based materials have shown promise for use in demanding optical applications, such as military use of high powered lasers. However, such materials are not without drawbacks, including material fabrication/processing issues. In this regard, the industry has sought to develop single crystalline spinel material, such as in the form of boules, from melt-based process techniques including the so-called Czochralski technique among others. Here, generally a stoichiometric crystal (typically $MgO \cdot Al_2O_3$, having an $MgO:Al_2O_3$ ratio of 1:1) is grown from a batch melt. While melt-based techniques have shown much promise for the creation of single-crystal spinel materials, the process is relatively difficult to control and suffers from undesirably low yield rates, thereby increasing costs. In addition, extended cooling periods and annealing periods are carried out to remove residual internal mechanical strain and stress present in the boules following boule formation. Such cooling rates may be unusually low, and cooling periods significantly long, affecting throughput and increasing thermal budget and cost. In a similar manner, the extended annealing times, which may range into the hundreds of hours, further increase processing costs.

[0005] Still further, even beyond the relatively high processing costs and despite the precautions taken in an attempt to address residual mechanical strain and stress in the crystal, oftentimes the wafers formed from boules tend to suffer from undesirably high failure rates, with frequently lower than 20% yield rates.

[0006] In view of the foregoing, it is generally desirable to provide improved spinel materials, well suited for optical applications, as well as improved methods for forming same.

SUMMARY

[0007] According to one aspect, a single crystal spinel material is provided, the material having a non-stoichiometric composition and having a transparency window represented by absorptivity over a wavelength range, the wavelength range extending from about 400

nm to about 800 nm. The transparency window is defined as the largest single absorptivity peak height along the wavelength range, the largest single peak height being not greater than 0.35 1/cm.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. 1 illustrates the optical transmission (absorptivity) properties of a previously developed cobalt-doped inverse spinel used in Q-switching applications.

[0009] FIG. 2 illustrates the optical transmission (absorptivity) properties of an alumina rich spinel, according to an embodiment of the present invention.

[0010] FIG. 3 illustrates a portion of the curve shown in FIG. 2.

Detailed Description

[0011] According to one aspect of the present invention, single crystal spinel materials, generally in the form of structural components, are provided. The single crystal spinel material generally has a non-stoichiometric composition and, according to one embodiment, has a transparency window over a wavelength range. The wavelength range generally extends along a transmission range from about 400 nm to about 800 nm. The transparency window may be defined as the largest single absorptivity peak height along the wavelength range, generally not greater than about 0.35 cm^{-1}. According to certain embodiments, the wavelength range is further extended, meaning that the transparency window is maintained over a wider frequency range. For example, the wavelength range may extend up to about 2000 nm such as 3000 nm, 3500 nm, or even 4000 nm. The above-noted largest single absorptivity peak height in certain embodiments is even further reduced, representing even superior transmittance properties, such as a height not greater than about 0.33 cm^{-1}, about 0.30 cm^{-1}, about 0.25 cm^{-1}, about 0.20 cm^{-1}, about 0.15 cm^{-1}, or even about 0.10 cm^{-1}.. Desirably, transmittance (or absorption) properties are fairly flat over an extended wavelength range,

indicating a lack of dependency of transmittance properties based upon wavelength or frequency.

[0012] The actual optical transmittance measurements are dependent upon various parameters.. Generally, optical transmittance data are taken from samples having a thickness within a range of about 5 to 10 mm, which samples are machined for parallelism, flatness and surface finish. Samples had a parallelism less than 10 seconds or 0.003 degrees, flatness of 1/10 wave maximum deviation over 90% of aperture as measured with a 632.8nm HeNe, and Mil spec, requiring scratch and dig specifications according to Mil-O-13830A, having a 20/10 finish. However, the reported absorptivity data are intrinsically normalized for thickness of the sample, that is, are generally thickness independent.

[0013] To clarify the foregoing optical properties, attention is drawn to the drawings herein. FIG. 1 illustrates the optical transmission data taken from a $MgO \cdot Al_2O_3$ spinel having a b:a ratio of 3:1, doped with 0.01% of Co^{2+}. This particular material was formed according to an embodiment described in U.S. Patent Application 09/863,013, published as U.S. 2003/0007520, commonly owned by the present assignee. This particular material is used for Q-switching applications, generally distinct from the optical applications according to embodiments of the present invention. As illustrated, the sample has a largest single absorptivity peak height of about 0.4 cm^{-1} occurring at about 590 nm.

[0014] In contrast, FIGS. 2 and 3 illustrate the optical transmission properties according to an embodiment of the present invention, namely an undoped $aMgO \cdot bAl_2O_3$ spinel having a b:a ratio of about 3:1. As illustrated, the sample has a fairly wide transmission window extending from about 400 nm to about 3700 nm. The largest single absorptivity peak is less than about 0.1 cm^{-1}, occurring at about 800 nm, represents a much smaller optical transmission loss or absorption than the cobalt-doped sample illustrated in FIG. 1. A similar absorptivity peak occurs at about 3000 nm.

[0015] Turning to fabrication of spinel materials, typically, processing begins with the formation of a batch melt in a crucible. The batch melt is generally provided to manifest

a non-stoichiometric composition in the as-formed spinel material, generally in the form of a "boule," describing a single crystal mass formed by melt processing, which includes ingots, cylinders and the like structures. According to one embodiment, the boule has a general formula of $aAD \cdot bE_2D_3$, wherein A is selected from the group consisting of Mg, Ca, Zn, Mn, Ba, Sr, Cd, Fe, and combinations thereof, E is selected from the group consisting Al, In, Cr, Sc, Lu, Fe, and combinations thereof, and D is selected from the group consisting O, S, Se, and combinations thereof, wherein a ratio b:a > 1:1 such that the spinel is rich in E_2D_3. For clarification, a stoichiometric composition is one in which the ratio of b:a = 1:1, while non-stoichiometric compositions have a b:a ratio $\neq$ 1:1.

[0016] According to certain embodiments, A is Mg, D is O and E is Al, such that the single crystal spinel has the formula $aMgO \cdot bAl_2O_3$. While some of the disclosure contained herein makes reference to the $MgO\text{-}Al_2O_3$ spinel based-compositions, it is understood that the present disclosure more generally relates to a broader group of spinel compositions, having the generalized formula $aAD \cdot bE_2D_3$, as described above.

[0017] While E_2D_3-rich spinels are generally represented by a ratio b:a greater than 1:1, certain embodiments have a b:a ratio not less than about 1.2:1, such as not less than about 1.5:1. Other embodiments have even higher proportions of E_2D_3 relative to AD, such as not less than about 2.0:1, or even not less than about 2.5:1. According to certain embodiments, the relative content of E_2D_3 is limited, so as to have a b:a ratio not greater than about 4:1. Specific embodiments may have a b:a ratio of about 3:1 (e.g., 2.9:1).

[0018] Following formation of a batch melt in a crucible, typically, the spinel single crystal boule is formed by one of various techniques such as the Czochralski pulling technique. While the Czochralski pulling technique has been utilized for formation of certain embodiments herein, it is understood that any one of a number of melt-based techniques, as distinct from flame-fusion techniques, may be utilized. Such melt-based techniques also include the Bridgman method, the liquefied encapsulated Bridgman method, the horizontal gradient freeze method, and edge-defined growth method, the Stockberger method, or the Kryopolus method. These melt-based techniques fundamentally differ from flame fusion techniques in that melt-based techniques grow a

boule from a melt. In contrast, flame fusion does not create a batch melt from which a boule is grown, but rather, provides a constant flow of raw material (such as in powder form), to a hot flame, and the molten product is then projected against a receiving surface on which the molten product solidifies.

[0019] Generally, the single seed crystal is contacted with the melt, while rotating the batch melt and the seed crystal relative to each other. Typically, the seed crystal is formed of stoichiometric spinel and has sufficiently high purity and crystallographic homogeneity to provide a suitable template for boule growth. The seed crystal may be rotated relative to a fixed crucible, the crucible may be rotated relative to a fixed seed crystal, or both the crucible and the seed crystal may be rotated. During rotation, the seed crystal and the actively forming boule are drawn out of the melt.

[0020] Typically, the boule consists essentially of a single spinel phase, with no secondary phases. According to another feature, the boule and the components processed therefrom are free of impurities and dopants. For example, Co is restricted from inclusion in the foregoing embodiment, which otherwise is a dopant for Q-switch applications. In contrast to Q-switch applications, it is generally desired that a relatively pure spinel is utilized substantially free of dopants that affect the basic and novel properties of the device substrates.

[0021] According to embodiments of the present invention, a single crystal spinel boule is formed having desirable properties. In addition to desired optical properties, the boules, and components formed therefrom also generally have reduced mechanical stress and/or strain, as compared to stoichiometric articles having a b:a ratio of 1:1. In this regard, embodiments of the present invention provide desirably high yield rates in connection with formation of single crystal components that form integral parts of larger scale optical assemblies, and also provide improved processing features, discussed in more detail hereinbelow.

[0022] With respect to improved processing features, the boule may be cooled at relatively high cooling rates such as not less than about 50°C/hour. Even higher cooling rates may be utilized according to embodiments of the present invention, such as not less

than about 100°C/hour, 200°C/hour and even at a rate of greater than about 300°C/hour. The increased cooling rates desirably improve throughput of the fabrication process for forming single crystal boules and further reduce the thermal budget of the entire fabrication, and accordingly reduce costs. Boules formed according to conventional processing generally are cooled at relatively low cooling rates, in an attempt to prevent fracture during the cooling process. However, according to embodiments of the present invention, the cooling rates may be substantially higher yet still provide intact boules in the as-cooled form. Generally, conventional cooling rates are on the order of 40°C/hour or less, requiring cooling periods on the order of days.

[0023] Still further, according to another embodiment of the present invention, annealing of the boule, conventionally carried out subsequent to cooling, is restricted to a relatively short time period. Typically, the time period is not greater than about 50 hours, such as not greater than about 30 hours, or even 20 hours. According to certain embodiments, the annealing is restricted to a time period not greater than about 10 hours. Indeed, annealing may be substantially completely eliminated, thereby obviating post-forming heat treatment. In contrast, conventional boule forming technology generally requires use of substantial anneal periods in an attempt to mitigate residual internal stress and strain, responsible for low wafer yield rates as well as boule fracture. Without wishing to be tied to any particular theory, it is believed that the reduction and internal stress and strain in the boule according to embodiments herein permits such flexible processing conditions, including decreased or complete elimination of annealing periods, as well as increased cooling rates as noted above.

[0024] According to another feature, the reduction in internal mechanical stress and strain are quantified by yield rate, the number of intact components formed by machining the boule. Typically, machining is carried out by any one of several slicing techniques, most notably wire sawing. As used herein, yield rate may be quantified by the formula $c_i/(c_i + c_f) \times 100\%$, wherein c_i = the number of intact components processed from the boule, and c_f = the number of fractured components from the boule due to internal mechanical stress or strain in the boule. Conventionally, this yield rate is very low, such as on the order 10%. The unacceptably low yield rate is a manifestation of excessive

internal stresses and strain in the boule. In contrast, yield rates according to embodiments of the present invention are typically not less than about 25%, 30% or even 40%. Other embodiments show increasingly high yield rates, such as not less than about 50, 60 or even 70%. Indeed, certain embodiments have demonstrated near 100% yield. This reduce internal mechanical stress and/or strain as quantified above is not only present within the as-formed (raw) boules, but also the processed boules, the component machined from boules. In this regard, the foregoing description of processed boules generally denotes boules that have been subjected to post-cooling machining steps, such as grinding, lapping, polishing and cleaning.

[0025] Turning to the particular physical manifestation of the spinel materials, embodiments may have various geometric configurations. For example, the material may be in the form of a polygonal planar window such as a rectangle or square. Alternatively, the component may be in the shape of a flat disc having a circular or oval outer periphery. Certain specialized applications call for more complex shapes, such as in the form of a cone or dome. Such components may be suitably utilized at the leading end of a laser guided missile, for example. Still other manifestations include light tubes, akin to fiber optic components. A particular application includes mirrors, having a highly polished surface oriented at a particular angle to reflect and/or transmit IR light, in applications such as in lasing devices, particularly including the laser cavity.

[0026] Turning to durability testing, various materials were tested in a controlled environment to determine user damage thresholds. Damage testing was carried out by the so-called least fluence failure technique, utilizing a nominal pulse width (FWHM) of 20 ns, at an incidence angle of 0°. The number of sites utilized for testing was varied, generally within a range of 60 to 90. Shots per site were also varied, generally within a range of about 50 to 200. According to an embodiment of the present invention, typically, the material has a laser damage threshold of not less than about 3.00 GW/cm^2 at a wavelength of 1064 nm. The laser damage threshold may even be higher, such as not less than about 3.25, or even 3.50 GW/cm^2 at a wavelength of 1064 nm

[0027] A first set of data was generated at a wavelength of 1064 nm. The spot diameter ($1/e^2$) was 430 microns. 80 sites were tested at a rate of 200 shots per site. Table 1 below summarizes the data of a 3:1 spinel according to an embodiment of the present invention, as contrasted against stoichimetric 1:1 spinel, as well as sapphire and YAG.

[0028] TABLE 1

MATERIAL	Damage Threshold @ 1064 nm (J/cm^2)	Damage Threshold @ 1064 nm (GW/cm^2)
Sapphire	38.6	1.93
YAG	28.0	1.40
1:1 Spinel	51.7	2.58
3:1 Spinel	80.0	4.00

[0029] As illustrated, the 3:1 spinel demonstrates superior damage resistance to laser exposure, notably demonstrating an unexpected damage threshold of 4.00 GW/cm^2.

[0030] Table 2 below summarizes the data for various samples at 1540 nm. The testing was carried out in a manner similar to the 1064 nm data. Here, the spot diameter was 115 microns. For the cobalt-doped sample, the spot diameter was 170 microns and 50 shots per site were utilized rather than 200 shots per site.

[0031] TABLE 2

MATERIAL	Damage Threshold @ 1540 nm (J/cm^2)	Damage Threshold @ 1540 nm (GW/cm^2)
Sapphire	36.7	1.8
YAG	65.9	3.3
1:1 Spinel	118.0	5.9
3:1 Spinel	67.6	3.4
1:3 Spinel Co^{2+}	63.5	3.2

[0032] Further, damage threshold testing was carried out at a wavelength of 532 nm. Again, testing was carried out in a manner similar to the 1064 nm testing unless otherwise indicated. Here, a spot diameter of 300 microns was utilized, a pulse width of 18 ns and the number of sites was increased to 100, while carrying out 200 shots per site.

[0033] TABLE 3

MATERIAL	Damage Threshold @ 532 nm (J/cm^2)	Damage Threshold @ 532 nm (GW/cm^2)
Sapphire	16.38	0.82
YAG	15.61	0.78
1:1 Spinel	44.97	2.25
3:1 Spinel	10.0	0.50

[0034] Still further, Table 4 below summarizes testing at 2100 nm. Testing was carried out at a pulse width of 40 ns, a spot diameter of 140 μm. 50 sites were tested, at a density of 200 shots/site.

[0035] TABLE 4

MATERIAL	Damage Threshold @ 2100 nm (J/cm^2)	Damage Threshold @ 2100 nm (GW/cm^2)
Sapphire	35.0	1.75
YAG	53.0	2.65
1:1 Spinel	60.0	3.0
3:1 Spinel	50.0	2.5

[0036] Still further, testing was carried out at 3000 nm. Testing was carried out at a pulse width of 10 ns, a spot diameter of 110 μm. 40 sites were tested, at a density of 200 shots/site.

[0037] TABLE 5

MATERIAL	Damage Threshold @ 3200 nm (J/cm^2)	Damage Threshold @ 3200 nm (GW/cm^2)
Sapphire	35.0	1.75
YAG	48.8	2.44
1:1 Spinel	>55.0	>2.75
3:1 Spinel	>55.0	>2.75

[0038] Example

[0039] Here, a specific process flow was utilized to create a single crystal spinel material according to an embodiment of the present invention.

[0040] Crucible Charge Preparation: 392.1g of MgO were combined with 2876.5g of Al_2O_3 (aluminum oxide). The raw materials were mixed together and heated for 12 hrs. At 1100 degrees centigrade in ceramic crucible. After cooling, the mixture was transferred into an iridium crucible 100 mm in diameter and 150 mm tall.

[0041] Crystal Growth: The iridium crucible with the oxide mixture was placed in standard Czochralski crystal growth station , and heated to the melting point of the oxide mixture by means of radio frequency heating. An inert ambient atmosphere consisting of nitrogen with a small addition of oxygen was used around the crucible.

[0042] After the mixture was liquid a small seed crystal of the 1:1 spinel with <111> orientation attached to the pulling rod was used to initiate the start of the crystal growth process. A single crystal boule was grown utilizing the following process conditions, diameter 53 mm, length 150 mm, seed pulling rate 2mm/hr, seed rotation rate 4 rpm, cool-down time 6 hrs, total time 123 hrs.

[0043] After cooling the crystal was visually inspected for bubbles, inclusions or any other visible defects. After visual inspection the top and bottom ends were removed, and crystal was subjected to an x-ray orientation check (Laue diffraction technique). After passing all inspection tests the crystal was ready for fabrication.

[0044] The foregoing description has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the scope to the precise form or embodiments disclosed, and modifications and variations are possible in light of the above teachings, or may be acquired from practice of embodiments of the invention.